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36

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Experimental Study of the Vibration of Acetylene Chemisorbed on Ni(111)

by

J. E. Demuth

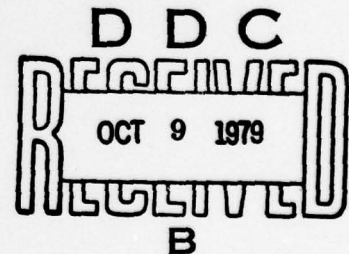IBM T. J. Watson Research Center
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previously by electron energy-loss spectroscopy for molecularly
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Experimental Study of the Vibrations of Acetylene Chemisorbed on Ni(111)*

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I. INTRODUCTION

High resolution electron energy loss spectroscopy (ELS) has become a powerful, practical method for obtaining chemical and geometrical information about chemisorbed species | 1 |. In this paper, we present and interpret ELS results for chemisorbed acetylene on Ni(111). Acetylene adsorption on transition metals surfaces has been studied by several experimental techniques including Photoemission, LEED, Thermal Desorption and ELS | 2-10 |. Our ELS studies of chemisorbed acetylene on Ni(111), as well as previous studies on Pt(111) | 5 | and W(100) | 6 |, show that the vibrations of chemisorbed acetylene are strongly shifted from those of the free molecule. Such frequency shifts can create significant ambiguities in assigning several of the important vibrational modes of the chemisorbed species. To minimize such uncertainties in our analysis we correlate our results to the vibrations of gaseous acetylene and a well-characterized transition metal complex of acetylene. From the vibrational frequencies of the assigned modes we find that contrary to early photoemission results | 2 |, chemisorbed acetylene is strongly rehybridized. Using these assignments together with symmetry considerations and the surface selection rule | 11 | we postulate a bonding geometry for acetylene on Ni(111) and compare this geometry to that deduced for acetylene on Pt(111) | 5 |.

II. EXPERIMENTAL PROCEDURES

Electron energy-loss spectroscopy was performed using a two-stage analyser/monochromator which typically provides an energy resolution of 65-80 cm^{-1}(8-10 meV) and a low, uniform background as described elsewhere | 5 |. A primary electron beam energy of 4.2 eV and a total scattering angle of 160° were chosen to optimize the loss signal. All loss measurements were made in the specular direction.

The Ni(111) crystal was spark cut from a single crystal boule into the form of a disk (~ 10 mm diameter and ~ 4mm thick) and mechanically polished. The sample was held by a Tungsten wire ring which nestled into a groove cut about the periphery of the disk. This

Tungsten wire was in turn mounted to the manipulator. The sample could be liquid nitrogen cooled ($T_{min}=140K$) and heated by electron bombardment of the rear side of the crystal. Temperatures were monitored via a Ni - 10%Cr/Ni thermocouple attached to the crystal.

The sample was pre-cleaned via high temperature (1100K) treatments in oxygen ($\sim$ 1 x 10^{-6} Torr) and then repolished to remove surface irregularities formed during this treatment. The sample was then remounted and subsequently cleaned using an initial oxygen treatment at low temperatures (<800K) followed by Argon ion sputtering (500V ion energy and 10 uA ion current). During Argon ion sputtering the crystal temperature was repetitively cycled between 300K and 1000K. The latter cleaning procedure is essentially that used in earlier studies [2,3]. Surface cleanliness and ordering were monitored by Auger electron spectroscopy and LEED, respectively. Reagent grade acetylene (99.9%) and its high purity deuterated counterpart were used and examined for impurities in-situ by mass spectroscopy. We note that although the pressures in the experimental chamber were typically about $1x10^{-10}$, we generally observed trace contamination of CO ($\leq$ 0.02 monolayers) on the sample after dosing.

III. EXPERIMENTAL RESULTS

In Figure 1, we show the vibrational loss spectra for a 3 x 10^{-6} Torr-sec (3 Langmuirs,L) exposure of acetylene (top) and deuterated acetylene (bottom) to Ni (111) at room temperature. This exposure gives rise to a p(2x2) LEED pattern. Further exposure at room temperature produces a second hydrocarbon phase with new peaks at ~780 and 2980 cm^{-1} for normal acetylene and 590 and 2160 cm^{-1} for deuterated acetylene, as described elsewhere [10]. Exposures at low temperature (T=140K) prior to multilayer condensation produce spectra similar to those in Fig. 1 with three minor exceptions. Namely, the weak loss feature at 680 cm^{-1} is more pronounced, the loss at 510 cm^{-1} (or 470 for deuterated acetylene) has a slightly lower intensity, and the shoulder on the ~1200 cm^{-1} loss at ~1400 cm^{-1} for normal acetylene is not visible. This latter feature is also coverage-dependent at room temperature.

In Fig. 1, we also show an enlarged section of the loss in the C-H stretching region obtained at low temperatures (T~200K) with coadsorbed deuterium. The full width of this peak at half maximum is the smallest when hydrogen or deuterium are coadsorbed (~10 cm^{-1} greater than the incident beam width of 80cm^{-1}). Without chemisorbed hydrogen or deuterium this peak widens to ~100 cm^{-1}. We also see no indication of the admixture of coadsorbed deuterium into the adsorbed molecule.

The large loss feature at ~1200 cm^{-1} is also broad and appears to be asymmetric. In Fig. 2 we show an enlarged section of this region obtained with a better signal to noise ratio. These spectra not only show the weak ~ 1400 cm^{-1} loss for normal acetylene but also a weak loss at 1065 cm^{-1}. (The corresponding weak peaks for deuterated acetylene are either shifted out of this range or obscured under the 1190 cm^{-1} loss.) As mentioned earlier, the intensity of the loss near 1400 cm^{-1} is variable and depends upon sample temperature and exposure-- effects which lead us to believe that this loss arises from small amounts of another species and not from chemisorbed acetylene.

The presence of coadsorbed hydrogen on the surface also effects the intensity of the ~1200 (1190) cm^{-1} loss relative to the other peaks. Namely, coadsorbed hydrogen reduces the intensity of the 1200 (1190) cm^{-1} loss feature by a factor of ~4 for normal acetylene and ~2 for deuterated acetylene. For chemisorbed acetylene formed from the dehydrogenation of ethylene on Ni(111) at room temperature, we also see the same pattern of relative intensity changes as observed in the presence of coadsorbed hydrogen. This confirms the presence of coadsorbed hydrogen after the dehydrogenation of ethylene as suggested elsewhere [12].

In general, coverage-dependent shifts in the observed losses were not significant and were not studied in detail. Variations of up to 10 cm^{-1} in peak positions did occur over the course of our studies but these may not be meaningful due to small changes in sample and spectrometer alignment. Therefore, the tabulated frequencies we present later represent mean values and are accurate to ~ ±5 cm^{-1}.

IV. INTERPRETATION

A. Vibrational Assignments

An assignment of some of the vibrational losses can be made straightforwardly by considering the spectra of normal and deuterated acetylene. In particular, the C-H (C-D) stretching modes must be assigned to the 2910 (2190) cm^{-1} losses while the loss features at 510 (470) cm^{-1} and 1220 (1190) must be related to the carbon derived modes, the C-M and C-C stretching modes, respectively. To make any further assignment requires additional information which we obtain from a well-characterized acetylene-transition metal compound $C_2H_2Co_2(CO)_6$. This particular acetylene compound is the only 3d-transition metal compound we know of which is both structurally and vibrationally (including a normal mode analysis) well characterized | 13,14 |. Although the relationship of this complex and its vibrations to chemisorbed acetylene on Ni can be questioned, it nevertheless provides a very useful guide in correlating and assigning the vibrations that we observe.

In Table I, we summarize the assigned vibrations of gaseous acetylene | 15 | and the acetylene-cobalt compound | 13 |, as well as the vibrational losses observed for chemisorbed acetylene on Ni(111). We also indicate the assigned vibrations for acetylene on Pt (111) | 5 | and ethylene di-chloride | 15 | for a later discussion. The symmetry assignments of the modes for this acetylene di-cobalt complex (C_{2v} symmetry) are also given.

The trends in frequency in going from gaseous acetylene, complexed acetylene and chemisorbed acetylene on Ni that are given in Table I, are illustrated in Figure 3. Here, the solid lines and dashed lines represent the frequency trends for normal and deuterated acetylene, respectively. The dotted lines show the frequency trends for deuterated acetylene which have been multiplied by the indicated factor to crudely account for isotopic frequency shifts. These trends confirm our initial assignment of the C-H, C-C and C-M stretching modes. We can also readily correlate the δ(C-H) in-plane-deformation modes. Although a weak loss observed at 680 cm^{-1} for normal acetylene on Ni could be related to an τ(C-H) out-of-plane deformation mode, it is most likely derived from minute amounts of adsorbed H_2O. (The

assignment of this vibrational loss as the τ(C-H) out of plane deformation mode also turns out to be inconsistent with our other assignments and the deduced geometry to be discussed later.)

Further support for these vibrational assignments occurs when we compare the frequency ratios of normal and deuterated acetylene for gaseous, complexed and chemisorbed acetylene. Here we observe a uniform trend in the ratios for these different states of acetylene. For example, the v(C-H)/v(C-D) ratios increase from 1.2491, 1.3209 to 1.3310; the δ_s(C-H) ratios increase from 1.2119, 1.2757 to 1.3462; while the v(C-C) ratios decrease from 1.1203, 1.0416 to 1.0167. Since the mass differential between Co and Ni is small, we might expect such trends to exist on a chemical basis.

B. Frequencies and Intensities

In making our vibrational assignments, we have not considered the magnitudes or detailed frequencies of the observed losses. Instead, we have depended upon isotopic shifts together with the general trends between chemically related states of acetylene. We now examine the frequencies and intensities of these assigned losses and consider their implications to the structure of chemisorbed acetylene.

The frequency shifts of both v(C-C) and v_s(C-H) vibrations indicate a strongly rehybridized species. This rehybridization is greater than occurs for acetylene in the first excited state, $^1A_\mu$, where both the geometry and vibrational frequencies have been established [16,17]. This latter geometry is generally characteristic of sp^2 hybridization with the hydrogen atoms in a planar trans-configuration and a C-C bond length of 1.38Å. The vibrations for the $^1A_\mu$ state were determined to be 3000 (2215), 1380 (1310) and 1049 (840) cm^{-1} for the symetric v(C-H), v(C-C) and δ(C-H) modes, respectively [16]. The similarities between the vibrations of the first excited state of acetylene and those for the cobalt-acetylene compound or chemisorbed acetylene raise many interesting questions related to the nature of bonding. This has been discussed for the acetylene compound previously [13,14] and is not considered here.

We can also relate the v(C-C) and v_s(C-H) frequencies observed for chemisorbed acetylene to those for C_2 hydrocarbons--a classical approach in infrared spectroscopy. These frequencies are shown in Fig. 4 plotted as a function of C-C bond length. If we directly correlate our frequencies for chemisorbed acetylene to those for free molecules, we expect a C-C bond length for chemisorbed acetylene between 1.47-1.54Å i.e., a bond length character-istic of $sp^{2.6}$ to sp^3 hybridization. However, one can question whether the bond order-bond frequency relationship commonly used for free molecules is directly applicable to adsorbed acetylene. This may arise for two reasons. First, the C-C vibration may occur so close to the surface that other interactions or solid state (e.g., screening) effects may also shift v(C-C) frequencies. Such an effect is certainly not large since both v(C-C) and v(C-H) vibrations correspond to similar states of hybridization. Secondly, the partial occupation of the π^* orbital of chemisorbed acetylene, which is believed to occur in bonding | 17-20 |, may modify the bond frequency/bond length relationship from that occurring in the ground-state molecule. This effect is suggested when we compare the vibrations and geometry for the $^1A_\mu$ state of acetylene. As shown in Fig. 4, the frequencies of $^1A_\mu$ acetylene are smaller than that expected on the basis of its C-C bond length. Although this difference may arise from uncertainties in the geometry of $^1A_\mu$ acetylene, such discrepancies may also limit the use of vibration / bond length relationships of free molecules to determine detailed geometric information. If we account for such discrepancies for the $^1A_\mu$ state we estimate a C-C bond length of 1.45-1.49Å for chemisorbed acetylene on Ni. This corresponds to a state of hybridization between $sp^{2.5}$-$sp^{2.8}$ and places a lower bound on the state of hybridization.

A detailed determination of the CCH angle for chemisorbed acetylene to corroborate this hybridization state would require an analysis of the observed intensities | 21 | which we do not do here. We hesitate in relating gas phase absorption measurements to the intensities observed for chemisorbed acetylene since the bonding to the metal atoms may alter the deduced "effective" ionic charges.

The bonding symmetry and the orientatation of chemisorbed acetylene relative to the Ni(111) surface can be deduced from the number and types of vibrations observed as well as the "surface selection rule" [11] that only modes with components of their dynamic dipoles normal to the surface will be strongly excited under our experimental conditions. From symmetry considerations, the presence of two δ(C-H) losses indicates that C_{2v} symmetry is broken. This, together with the fact that coadsorption with hydrogen narrows the CH stretching frequency and reduces the intensity of the CC stretching loss, implies that the initial chemisorbed state of acetylene has its molecular axis inclined relative to the surface. We note that the intense ν(C-C) loss and the weak 1400 cm^1 loss (a possible CH$_2$ scissor vibration) could be interpreted to indicate the presence of a C=CH$_2$ species bonded end on to the surface analogous to new species observed on Pt(111) [4]. However, the weak loss at 1400 cm^{-1} was not always observed at lower temperatures despite the presence of all other losses. Also, the adsorption of normal acetylene onto a surface with preadsorbed deuterium, or the adsorption of deuterated acetylene onto a surface with preadsorbed hydrogen, did not show any isotopic mixing as found on Pt(111) [4]. In view of these results and the excellent correlation of the vibrations shown in Table I and Fig. 3, we rule out such vinyl type species.

Further information about the degree of inclination of the C-C bond axis to the surface is contained in the CH stretching vibrations. The CH stretching loss is broadened but not split into two distinct CH stretching frequencies. This indicates that the differences in the environment of the two CH groups is not be too great and suggests only a small angle of inclination. A small angle of inclination might at first appear to be inconsistent with the intense C-C loss observed. However, from calculations of the dynamic dipole of acetylene bonded to Be clusters, it is found that a large dynamic dipole can occur due to the charge that couples to the metal atoms [22]. Here, vibrations of the C-C bond of acetylene which lies "flat" on the cluster can induce large dynamic dipoles perpendicular to the C-C bond axis. Thus, a strong excitation of C-C vibrational modes may occur even if the C-C bond axis of acetylene were to lie flat on the surface.

Although we can predict the general orientation of acetylene on the surface, its location on the surface is less certain from our results. The strong rehybridization and smaller v(C-M) frequency than occurs for the di-cobalt compound argue for the bonding of acetylene to high coordination sites on the surface. Such a site would also have to facilitate the afore-mentioned molecular orientation. One such bonding geometry is shown in Fig. 5 (a). This geometry is consistent with the observed LEED pattern and the observed manner of formation of CH species on Ni(111). | 3 | Such a geometry is also analogous to that determined for organometallic alkyne compounds where the alkyne is coordinated to two metal atoms (μ-bonded) as in $C_2H_2Co_2(CO)_6$ | 13 | and other compounds | 23-24 |, or coordinated to three metal atoms in a pyrimidal four metal atom cluster | 25-26 |. For our proposed geometry, the electronic inequivalence of the two three fold hollow sites on Ni(111) would naturally lead to an inclination of chemisorbed acetylene and our ability to observe both δ(C-H) modes. If we consider a steric model which used our deduced C-C bond lengths of 1.45-1.49Å (1.54Å) and assume the carbon atoms lie directly above each three fold hollow site, we determine an inclination of 10-17° (22°), respectively. In Fig. 5a, we arbitrarily show an angle of inclination of 20°.

C. Comparison to Acetylene on Pt(111)

Vibrational loss spectra have also been measured and interpreted for acetylene chemisorbed on Pt(111) at low temperatures | 4 |. Under these conditions, acetylene is associatively chemisorbed prior to subsequent reactions with the surface at higher temperatures | 4,27 |. The vibrational losses for chemisorbed acetylene on Pt(111) and their assignments are shown in Table I and are generally consistent with the trends in the frequencies we observe for free acetylene and complexed acetylene. (We note the poor correspondence of the vibrations of ethylene di-chloride to chemisorbed acetylene on either Ni or Pt.) In comparing the v(C-C) and v(C-H) frequencies for chemisorbed acetylene on Pt(111) and Ni(111), acetylene on Pt(111) appears to be a less rehybridized molecule than on Ni(111). The strikingly different relative intensities of the v(C-C) and τ(C-H) modes as well as the frequen-

cy differences in the δ_s modes on Ni and Pt suggest that different molecular orientations occur. The model geometry which best describes the orientation of chemisorbed acetylene on Pt(111) is shown in Fig. 5b and was originally proposed by Ibach and Lehwald | 5 |. Alkyne organometallic complexes bonded to three metal atoms exist which have the carbon atoms in a similar bonding orientation to that shown in Fig. 4b | 28,29 |. Interestingly, ab-initio Hartree-Fock LCAO SCF calculations of acetylene bonded to Be_3 clusters in a location similar to that shown in Fig. 4b indicate that the plane of the molecule also prefers to be skewed to the surface of the cluster as shown in Fig. 4b | 22 |.

V. DISCUSSION AND SUMMARY

In our analysis, we have considered the implications of the adsorbate/surface symmetry as well as the surface selection rule, but we do not explicitly exclude surface selection rule "forbidden" modes in our assignments. We cannot rule out the possibility that weak loss features may arise from non-dipole (short range) excitations | 30-32 | or from other effects associated with bonding to the surface atoms. However, the observed modes and our assignments are consistent with the presence of a surface selection rule. This is not surprising considering that we choose experimental conditions which are expected to preferentially favor optical (long range) excitations. | 30 |.

The vibrational frequencies we observe for chemisorbed acetylene are strongly shifted from those of the free molecule. Both isotopic shifts and a correlation of frequencies to those of gaseous acetylene and an acetylene-cobalt compound are used to assign the vibrations. The frequency shifts we measure for the ELS active vibrations of chemisorbed acetylene (see Fig. 3) are also physically plausible. The C-C and C-H stretching vibrations are reduced due to the rehybridization of the molecule caused by bonding to the surface. The increased frequency of the in-plane C-H deformation modes can arise from a stiffening of these force constants associated with the bonding to the surface. Finally, the reduced C-M frequency can arise from the higher coordination possible on the surface than in the di-cobalt compound.

Our results indicate that chemisorbed acetylene on Ni(111) is strongly rehybridized ($sp^{2.5}$-$sp^{3.0}$) and suggest a particular bonding geometry analogous to known organometallic alkyne compounds. We note that in our analysis we have avoided describing the nature of the bonding in terms of π or di-σ modes of bonding. As found in acetylene-Be cluster calculations, such designations can be difficult to make based upon the geometric orientation alone | 22 |. Our proposed bonding geometry has the carbon atoms residing almost directly above two adjacent three-fold hollow sites and at slightly different distances above the surface. The hydrogen atoms are strongly bent back and pointed away from the surface. Such a geometry, and particularly the inclination of the C-C bond axis relative to the surface, is consistent with recent calculations by Anderson | 33 |. This strongly distorted C_2H_2 species is also consistent with the C-C bond breaking observed in forming CH species from acetylene on Ni(111) | 3 |, but appears contradictory to early photoemission studies | 2-4 |. In those studies the close similarities of the higher lying ionization levels of chemisorbed hydrocarbons on Ni relative to their gas phase counterparts lead to the conclusion that only small distortions occurred | 2 |. Although a more detailed analysis of the geometry-induced level shifts of acetylene supported this conclusion | 4 |, both of these early conclusions concerning acetylene were uncertain due to the limited number of levels experimentally observed. The recent observation of the lower lying ionization levels of these species with filtered hν=40.8eV radiation | 34 | prompted a new analysis which concluded that a strongly distorted acetylene species was also consistent with the observed photoemission levels.

The differences in the state of hybridization and the bonding geometries of acetylene chemisorbed on Ni(111) and Pt(111) are interesting. Such differences are also likely related to the differences in the reactions of acetylene on Ni and Pt(111). Namely, heating chemisorbed acetylene on Ni(111) causes dissociation at ~ 400K and leaves atomic carbon | 3 | while on Pt(111) vinyl-like species form above ~ 300K | 4,5,27 |. The difference in bonding geometry may arise from two related but distinct sources. The first is a geometric effect associated with the differences in the surface lattice constants of Ni and Pt

$(d_{Ni-Ni}=2.48\text{Å}, d_{Pt-Pt}=2.78\text{Å})$. Namely, the greater distance between adjacent three-fold hollow sites on Pt(111) (1.60Å) than on Ni(111) (1.43Å) may not allow for the optimal overlap of adsorbate and substrate wavefunctions. This may favor another high coordination bonding orientation on Pt. Secondly, these different geometries may arise from the difference in the character of the wavefunctions of Ni and Pt, i.e., the tail of the Ni wavefunction is more s-like and less d-like than Pt. Other evidence supports this latter possibility [35-38].

Other recent studies of acetylene coadsorbed with hydrogen on Ni(111) (formed from the decomposition of ethylene) show similar vibrations to those observed here, modulo some small differences in the frequencies and relative intensities [39]. These studies assign the frequencies on the basis of a normal mode analysis for a bonding site analogous to that shown in Fig. 4b (Other bonding orientations were not considered.) This gives rise to a different assignment of the vibrations than found here and leads to significant discrepancies between the observed and the expected intensities based on the surface selection rule.

An interesting comparison of our ELS results for chemisorbed acetylene can be made to IR studies of matrix isolated acetylene Ni cluster compounds formed under cryogenic conditions. Preliminary results on mono-Ni compounds indicate a weakly rehybridized acetylenic species [40]. Whether this phase is a precursor to a more strongly adsorbed species or a result of the minimal coordination possible with one Ni atom remains to be determined. Theoretical calculations for acetylene bonded to one nickel atom also indicate a weakly distorted species; however, multiply bonded structures involving several Ni atoms have not yet been theoretically investigated [37].

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Table I Vibrational mode assignments for free, complexed and chemisorbed acetylene (deuterated acetylene) on Ni(111) and Pt(111). The relative intensities for the chemisorbed species are indicated.

		FREE [a] C_2H_2	COMPLEXED [b,c] $C_2H_2Co_2(CO)_6$	$C_2H_2/Ni(111)$ (+5cm^{-1}) [c]	$C_2H_2/Pt(111)$ [d]	H–C≡C–Cl / Cl–C=C–H [e]
ν(C-H)	– sym	3374 (2701)	3116 (2359)A_1	2915m (2190m)	3010m (2245m)	3160
	– asym	3287 (2427)	3086 (2297)B_2	----	----	3086
ν(C-C)		1974 (1762)	1403 (1347)A_1	1215s (1195s)	1310w (1260m)	1591
δ(C-H)	– sym	612 (505)	768 (602)A_1	875m (650m)	985m (730m)	1179
	– asym	729 (539)	894 (751)B_2	1065w (880w)	----	1303
ν(C-M)	– sym	---	605 (561)A_1	505m (470m)	570m (----)	857
	– asym	---	551 (520)B_2	---	340w (310w)*	711
τ(C-H)	– sym	----	----	---	770s (570s)	570
	– asym	----	----	---	----	406
ν(M-M)		----	207 A_1	----	----	----

* Originally assigned as a second type of ν (C-M) mode.

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c. Yuji Iwashita, Inorg. Chem 9 1178 (1970).
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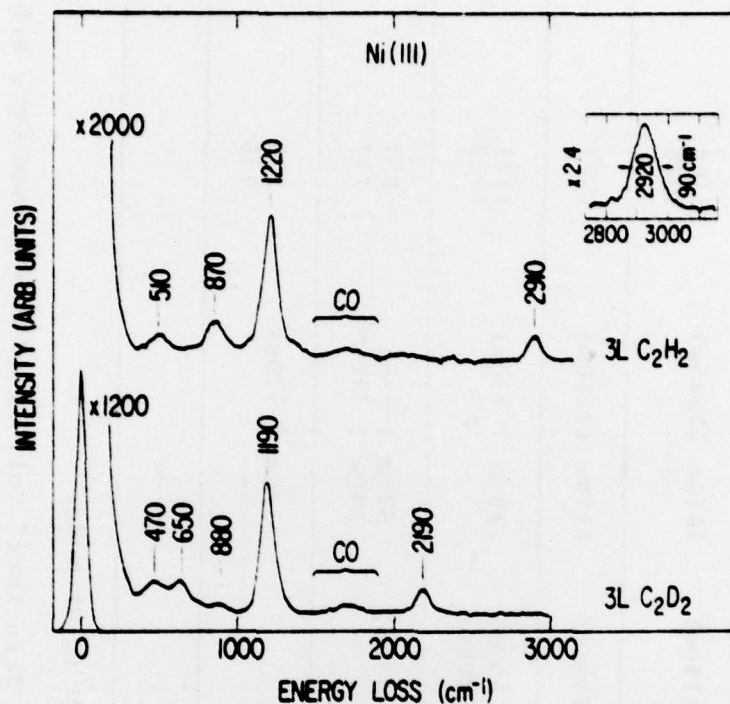e. Refr. 1, Page 330.

Fig. 1: The vibrational loss spectra for a 3×10^{-6} Torr-second exposure (3L) of normal acetylene (top) and deuterated acetylene (bottom) to Ni(111) at room temperature. The insert shows an expanded view of the C-H stretching region for acetylene coadsorbed on Ni(111) with deuterium at T~200K.
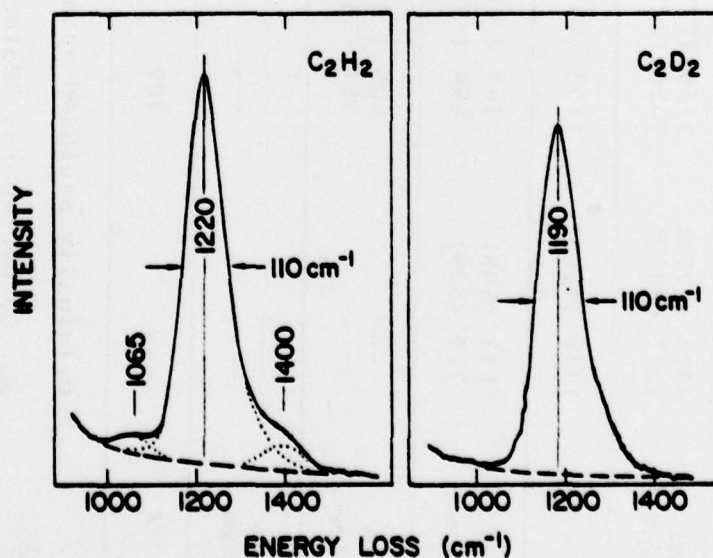

Fig. 2: Expanded section of the vibrational loss spectra about ~1200 cm^{-1} for a 3×10^{-6} Torr-second exposure of normal acetylene (right) and deuterated acetylene (left) to Ni(111) at room temperature. These spectra were obtained after cooling the sample to ~140K.

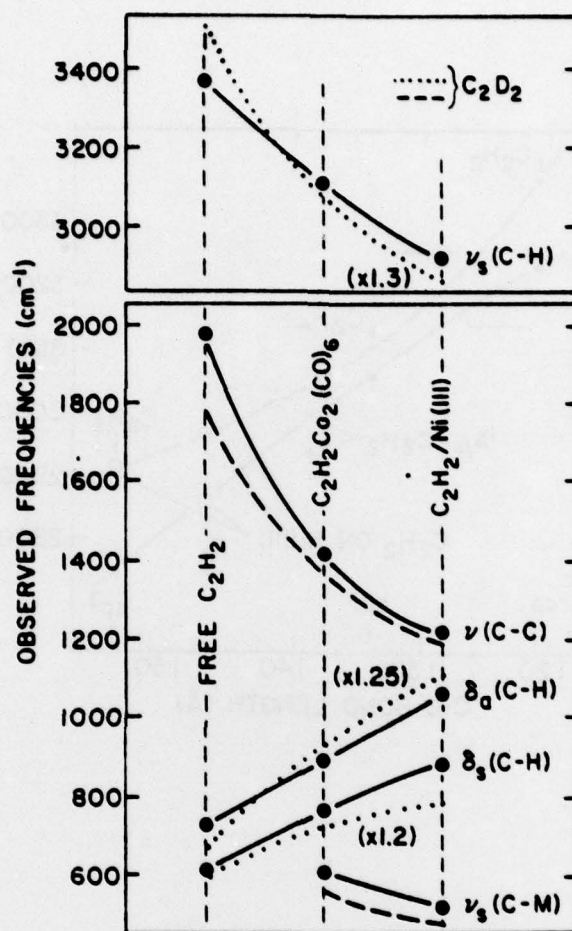Fig. 3: Correlation diagram of the vibrational modes of the acetylene molecule in the gas phase, in an organometallic di-cobalt compound and chemisorbed on a Ni(111) surface. The solid lines and dashed lines correspond to the frequencies for normal and deuterated acetylene. The dotted lines show the frequencies for deuterated acetylene after being scaled by the indicated factor so as to crudely account for isotopic shifts.
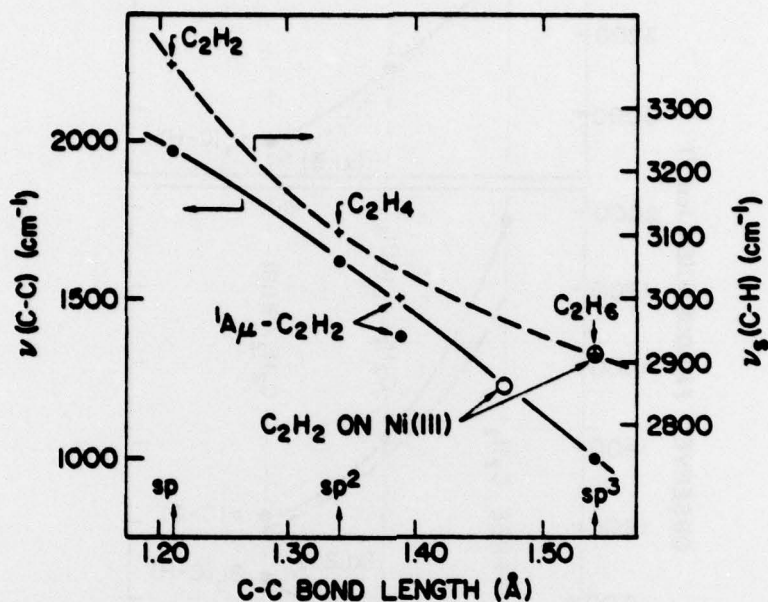
Fig. 4: Observed symmetric C-H (+) and C-C (•) stretching frequencies for gaseous C_2H_2, C_2H_4 and C_2H_6 plotted verses C-C bond length. The frequencies for the $^1A\mu$ state (first excited state) of free acetylene are noted while those observed for chemisorbed acetylene on Ni(111) are indicated by the open circles.

TOP VIEW

SIDE VIEW

(a)   (b)
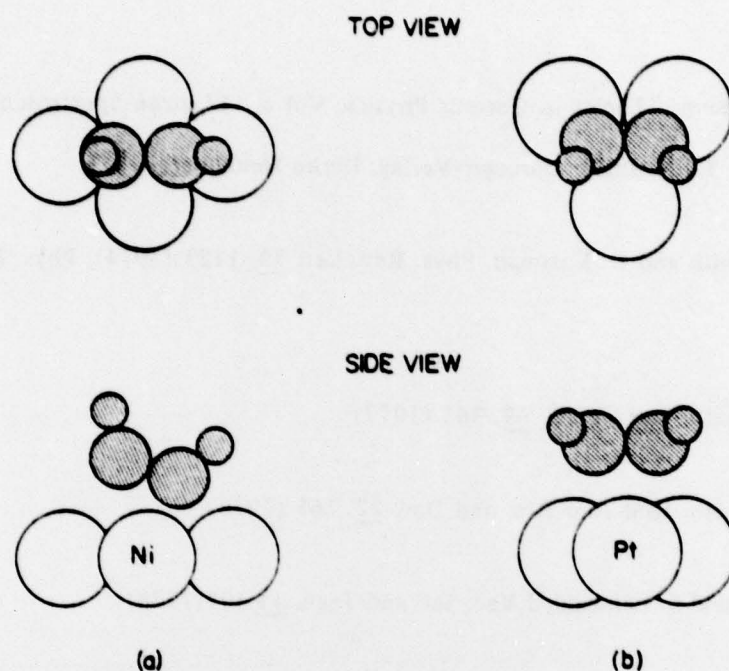
Fig. 5: Proposed bonding geometry and molecular orientation for (a) acetylene on Ni(111) and (b) acetylene on Pt(111). For geometry (a) the hydrogen atoms are bent strongly away from the C-C axis and the two carbon atoms lie at slightly different heights above the surface. (The molecular plane of acetylene is normal to the surface.) For geometry (b) the carbon atoms lie along a line parallel to the surface while the molecular plane of acetylene is inclined at some angle to the surface.

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